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THE DETERMINATION OF BACKGROUND LEVEL OF HEAVY METALS IN LEBANESE SOILS USING PARTICLE INDUCED X-RAY EMISSION TECHNIQUE

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SUMMARY

The background levels of heavy metals (As, Cu, Ni, Pb and Zn) were determined in 104 representative soil samples derived from 42 soil profiles representing the region of North Lebanon. The area of study, which is 602.6 km², represents 5.7 % of the total area of Lebanon and mainly consists of arable land: Akkar plain, Halba plateau and the surrounding hills.

The soil samples were taken from the soil surface and subsoil horizons reflecting the original parent material and the soils were classified into 4 groups in relation to their original parent materials. The obtained samples were crushed then pressured in order to obtain tablets. Afterward, the samples were covered with a very thin layer of ultra pure carbon and then passed to PIXE analysis in order to determine the concentration of the heavy metals.

This technique was based on the ionization of the sample atoms by the incidence of a proton beam and the subsequent emission of X-Rays characteristics of the elements present in the soil sample.

After building a comparison between the contamination classes set by Eickmann & Klocke with data obtained from this study, it was noticed that the

background levels of zinc, lead and arsenic were integrated within the multifunctional land use class. As for copper, only soils derived from volcanic rocks indicated a value of 56.5 mg/kg that exceeded the multifunctional land use class.

Finally, regarding nickel, all groups of soils indicated background values that exceeded the multifunctional land use class and were identified as: 116.5 mg/kg in the group of soils derived from volcanic rocks, 115.3 mg/kg in the group of soils derived from soft limestone, 60mg/kg in the group of soils derived from hard limestone and 52 mg/kg in the group of quaternary arable soils.

The results indicated different patterns of metals accumulated in the soils likely due to erosion-deposition process, land use operations, soil type as well as the original parent material.

This work represents the first large-scale study on heavy metal background and contamination status in Lebanese soils. Future research should focus on the adaptation of local criteria of soil pollution. These could be based on soil-heavy metal interaction and heavy metal bioavailability and pedotransfer, using the European standards in order to elaborate land use planning and zoning.

Key words: soil, heavy metals, PIXE, background value, contamination.

RÉSUMÉ

Les valeurs de fond des métaux lourds (As, Cu, Ni, Pb et Zn) ont été déterminées dans 104 échantillons de sol représentatifs, dérivés de 42 profils représentant la région du Nord du Liban. La région d'étude, qui est de 602,6 km², couvre 5,7 % de la surface totale du Liban et consiste principalement de terres arables: vallée de Akkar, plateau de Halba et les montagnes voisines.

Les échantillons ont été prélevés des horizons de surface et de profondeur, réagissant avec la roche-mère, et les sols ont été classifiés selon 4 groupes en fonction de leur roche-mère. Les échantillons obtenus ont été écrasés puis pressés afin d'obtenir des tablets. Ensuite, leur surface a été couverte par du carbone ultra pur et analysée par PIXE (Proton Induced X-Ray Emission) dans le but de déterminer la concentration des métaux lourds.

Cette technique a reposé sur l'ionisation des atomes de l'échantillon à analyser par l'incidence d'un faisceau d'ion H⁺ et l'émission ultérieure de rayons X caractéristiques des éléments présents dans cet échantillon.

Après avoir établi une comparaison entre les classes de contamination définies par Eickmann et Klocke avec les résultats obtenus dans cette étude, on a remarqué que le zinc, le plomb et l'arsenic ont été intégrés dans la classe d'usage multifonctionnel des terrains. Concernant le cuivre, uniquement les sols dérivés des roches volcaniques ont indiqué une valeur de 56,5 mg/kg qui a légèrement surpassé la classe d'usage multifonctionnel des terrains.

Enfinement pour le nickel, tous les groupes de sols ont indiqué des valeurs excédant la classe d'usage multifonctionnel des terrains et ont été identifiés comme suit: 116,5 mg/kg pour le groupe de sols dérivés des roches volcaniques, 115,3 mg/kg pour le groupe de sols dérivés des roches calcaires tendres, 60 mg/kg pour le groupe de sols dérivés des roches calcaires dures et 52 mg/kg pour le groupe des sols arables quaternaires.

Les résultats indiquent différents modèles d'accumulation des métaux dans les sols, étant influencés par les phénomènes d'érosion et de déposition, l'usage des terrains, la nature des sols ainsi que la roche-mère.

Ce travail est la première étude à grande échelle effectuée sur la valeur de fond et l'état des métaux lourds dans les sols du Liban. La future recherche doit reposer sur l'adaptation des critères locaux de contamination des sols. Ceci peut être basé sur l'interaction sol-métaux lourds, leur phytotoxicité et le risque de lessivage, utilisant des critères européens pour élaborer un zoning et une planification de l'utilisation rationnelle des terres.

Mots clés: sol, métaux lourds, PIXE, valeur de fond, contamination.

INTRODUCTION

In the soil, the concentration of trace metals, which are non-biodegradable, are increasing in an unescapable way and these contaminations cause the disturbance of the soil-plant-animal system (Morel *et al.*, 1998).

In Lebanon, there is very limited information on soil contamination concerning toxic heavy metals, which makes soil contamination assessment a difficult task.

Therefore, the 1st goal of this project is to determine the natural occurrence and obtain data on heavy metal concentrations in the soil units of North Lebanon, as to compare these values to the multifunctional land use and contamination classes set for Europe.

Objectives of this work also include:

- Using the GIS technique to facilitate the evaluation of heavy metals, and
- Applying (PIXE) Proton Induced X-Ray Emission technique for soil analysis, which is a non-destructive method used for the first time in Lebanon.

MATERIALS AND METHODS

One hundred and four representative soil samples derived from 42 soil profiles representing the region of North Lebanon were studied. These samples were available at the National Center for Remote Sensing, within the framework of the soil-mapping project (Darwich *et al.*, 2000) and covered the soil surface and subsoil horizons.

The area of study is located in North Lebanon and expands over 602.6 km². Geographically, it extends from the Mediterranean Sea in the West to the Syrian border in the East and is limited by Al Kabir River in the North, which separates the Lebanese and the Syrian territories.

The landform of the area consists of a level quaternary plain in the west and of Halba undulating plateau that consists of several basaltic hills.

Precipitations in the area of study are of 700-800 mm in Halba plateau and Akkar plain, and of 600-700 mm in the eastern part of the hills bordering the Syrian regions (Ministère des travaux publics et des transports, 1982). The extreme altitude is of 1632 m (C.A.L., 1977).

The area of study mainly consists of arable land. In addition to oak and pine forests, the land cover consists of field and vegetable crops on the coastal plain and of vegetable and fruit trees on the plateau (FAO, 1990).

In the laboratory of the Lebanese Commission of the Atomic Energy, the samples were crushed using an agate mortar then pressured in combination with boric acid in order to produce tablets.

Afterwards, their surface was covered with a very thin layer of ultra pure carbon in order to ensure a good electrical conductivity of the matrix surface.

After the carbon deposit, the sample was stuck directly on a target holder out of pure aluminum and became ready for PIXE analysis.

PIXE technique is based on the ionization of the sample atoms by the inci-

dence of a beam that interacts with the atoms present in the sample and excites them. These atoms will be de-excited thereafter by the emission of a characteristic X-Ray with a well defined energy. These rays were collected and detected by an X-Ray detector Si-Li, which was connected to a card in the computer and made it possible to have a spectrum representing the chemical elements of the sample (Johansson *et al.*, 1988).

The Eickmann & Klocke concept evaluates possible uses of soil contamination, which prevails in Europe (Eickmann & Klocke, 1993).

Figure 1 shows a model for possible uses of contaminated arable soils.

- (A) Refers to the BWI contamination class where low levels of hazardous elements are protected and the soil is suitable for multifunctional land use. The threshold to the next group is referred to the "precaution level" that indicates a certain probability of future problems.
- (B) Refers to the BWII contamination class where low levels of hazardous elements are tolerated, but the cropping must be adapted to the different extends of soil contamination. The threshold to the next group is the "trigger level", which focuses on special land use.
- (C) Refers to the BWIII contamination class, which is a safety interval that tolerates a higher level of hazardous elements, but the cropping must be adapted to the site and the "asset- to -preserve". The threshold to the next group is the "interventional level", which leads us to the last interval (C) where land reclamation is strictly demanded.

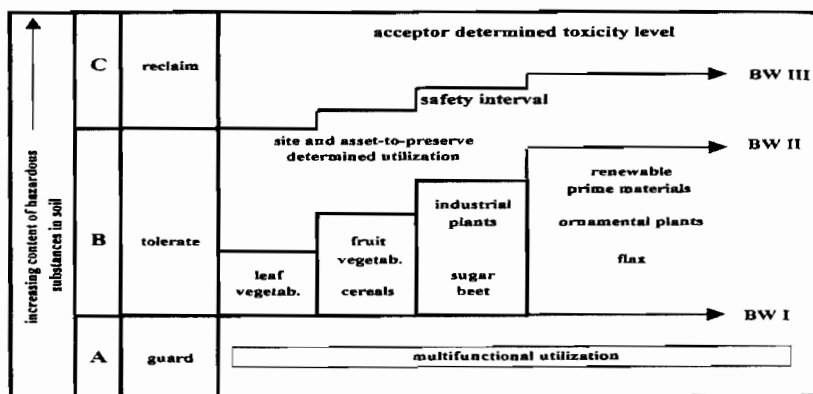


Figure 1. Step model for the utilization of contaminated soils for plant production. (Eickmann & Klocke, 1993) BW= Soil Value

Accordingly to Eickmann & Klocke (1993), the multifunctional land use class or BWI contamination class is set to less than 40 ppm for Ni, less than 50 ppm for Cu, 150 ppm for Zn, 20 ppm for As and 100 ppm for Pb.

RESULTS AND DISCUSSION

In order to follow the impact of the geology on heavy metal accumulation, soils investigated in our study were grouped according to their lithology classes under the following groups:

Quaternary arable soils, soils derived from soft limestone, soils derived from hard limestone and soils derived from volcanic rocks.

General characteristics of the soils of North Lebanon

1. Clay content

Clay content in the soils of North Lebanon is relatively low. However, in the group of soils derived from hard limestone, soft limestone and quaternary arable soils, most of the soils are rich in clay slightly exceeding 31%. Hence, heavy metal availability could be low in most of these heavy soils due to adsorption of heavy metals by clay. However, in the group of soils derived from volcanic rocks, most of the soils are low in clay, which probably makes heavy metal availability high.

2. Carbonate content

The majority of the area retains carbonate content below 25 % thus contributing to a low retention capacity and this is more evident in the group of soils derived from basalt and hard limestone, which promotes leaching of CaCO_3 . Similarly, in the group of quaternary arable soils, most of the soil profiles are non-calcareous and those derived from soft limestone are very slightly calcareous.

3. Content of pH

Regarding pH content, the majority of the soils under study are neutral and weakly basic having a pH value higher than 7.5 except for the group of soils derived from volcanic rocks that retains some weakly acid reaction. Therefore, metal availability could be low in these basic soils except for the last group.

4. Organic matter

The main soil units in the area of study are relatively rich in organic matter, which exceeds 3%. This organic matter induces metal adsorption and chelation, thus preventing its uptake by plants. However, a significant part of the quaternary arable plain is differentiated by low organic matter content being less than 2% given the current land management system. Therefore, frequent cultivation of the soils enhances the mineralisation of the organic matter.

As a result, the soil vulnerability was concluded in the studied 4 groups under study. Despite their high organic matter content, most of the soils derived from volcanic rocks are relatively low in clay and carbonate content and some profiles are weakly acidic. As a result, this group of soils could be possibly classified as being "vulnerable".

Despite the fact of being non-calcareous, most of the soils derived from the group of quaternary arable soils have high clay and organic matter content and retain high pH values. Thus they could be classified as being relatively of "low vulnerability".

Soils derived from hard limestone are non-calcareous but contain high clay and organic matter content as well as high pH values. In this manner, they are categorized as being relatively of "low vulnerability".

Most of the soils derived from soft limestone are very slightly calcareous and have moderate clay content and high organic matter content. Moreover, they are distinguished by high pH values. Consequently, soils of this group are possibly of "very low vulnerability".

Background value of heavy metals in the soils investigated in North Lebanon

Building a simple comparison between the multifunctional land use classes set by Eickmann & Klocke (1993) and data obtained from this study, shows that these values could be adjusted to Lebanese soils, to some extended.

When analyzing, for example the background value of Zinc for all groups of soils, it is observed that all corresponding levels remain below 150 ppm (Tab. 1), thus falling within the BWI contamination class. This also applies to Lead (Tab. 2) and Arsenic (Tab. 3).

Table 1: Background value of Zinc in mg/kg.

Parent Material	Zinc (mg/kg)	
Soft Limestone	112	Ap (0-30)*
Hard Limestone	83	A (0-25)*
Volcanic rocks	22.8	Ap (0-18)*
Quaternary arable soils	63.7	IIIA (52-110)*

*Horizon depth in cm

Table 2: Background value of Lead in mg/kg.

Parent Material	Lead (mg/kg)	
Soft Limestone	12.3	AC (30-45)*
Hard Limestone	8.4	Ap (0-15)*
Volcanic rocks	0	C (35-150)*
Quaternary arable soils	0	B ₂ (90-130)*

*Horizon depth in cm

Table 3: Background value of Arsenic in mg/kg.

Parent Material	Arsenic (mg/kg)	
Soft Limestone	4.3	AC (30-45)*
Hard Limestone	6.6	A (0-25)*
Volcanic rocks	0	C (25-70)*
Quaternary arable soils	0	Ap (0-30)*

*Horizon depth in cm

As for Copper, it is noted that soils derived from soft limestone, hard limestone and quaternary arable soils maintain background values included within the BWI class (Tab. 4). However, soils derived from volcanic rocks, being of high vulnerability, slightly surpass the BWI class limit and can be of some environmental concern

Table 4: Background value of Copper in mg/kg.

Parent Material	Copper (mg/kg)	
Soft Limestone	34.9	Ap (0-30)*
Hard Limestone	6	Ck (74-120)*
Volcanic rocks	56.5	C (150-230)*
Quaternary arable soils	12	A ₁₃ (22-42)*

*Horizon depth in cm

Regarding Nickel, soils derived from hard limestone and quaternary arable soils indicate values referring to the BWII contamination class but imply no immediate contamination hazard due to their low vulnerability (Tab. 5). However, soils derived from soft limestone and volcanic rocks imply much higher values and refer to the BWIII contamination class but only soils derived from volcanic rocks are of major concern because this group of soils is classified as being vulnerable.

Table 5: Background value of Nickel in mg/kg.

Parent Material	Nickel (mg/kg)	
Soft Limestone	115.3	B (12-30)*
Hard Limestone	60	Ck (74-120)*
Volcanic rocks	116.5	A (0-20)*
Quaternary arable soils	52	IIC (70-143)*

*Horizon depth in cm

Moreover, it would be interesting to point out that no mercury was found in the soils of North Lebanon as values of 0 mg/kg were recorded in all investigated soils.

Heavy metals in the Ap horizon

The investigation of heavy metals in the Ap horizon is very important in order to determine the degree of contamination hazard attributed to the soil-plant-animal system.

It can obviously be stated that very high amounts of Ni prevailed in most of the soils of North Lebanon. 80% of high concentrations coincided with volcanic rocks and a very high level was spotted at Hnaydir where the landform plateau reveals no depositions from any surroundings, no intensive agriculture and no source of industry. Therefore, this very high level of Ni is strictly geogenic. As for the high Ni concentrations found in the coastal quaternary plain, these were due to the presence of unconsolidated materials derived from volcanic rocks by erosion-deposition process. Similarly, in the group of soils derived from hard limestone, the Ni content was high due to the river loadings which originated from the volcanic rocks. On the other hand, low Ni contents in the soft limestone area coincided with the prevailing soft marly rocks that seemed to be poor in heavy metal content.

Regarding Pb distribution in the Ap horizon, nearly all soils investigated stand in the BWI class. However, due to its high energy, Oustwan River probably carries this heavy element from the volcanic rocks and promotes a high Pb deposit on the first meander of the river.

Cu content in the Ap horizon revealed that most of the soils investigated belong to the BWII class and a clear correlation between Cu and Ni distribution was noticed. High metals prevail in volcanic rocks and low metals in marl. There is also an erosion-deposition process from the volcanic rocks towards the coastal quaternary plain and the grouping of hard limestone.

Regarding Zn distribution, most of the soils analyzed belong to the BWII contamination class. Low levels were located on the coastal plain whereas high levels coincided with regions of high altitude that could witness weak movements with in the redistributed soil particles.

Most of the analyzed soils were classified within the multifunctional land use class for As but high point sources could most probably be related to an induced contamination.

Heavy metal distribution within the soil profiles

The study focused on the importance of the depth parameter in order to follow heavy metal distribution.

- In the group of quaternary arable soils, Ni, Cu and Zn were mostly characterized by a metal increase in the middle of the soil profile whereas As and Pb revealed a low homogeneous distribution.
- In the group of soils derived from hard limestone, Ni distribution was mostly differentiated by an increase in the middle of the soil profile whereas Cu was characterized by a homogeneous distribution with high content. The truncation of soils resulted in Zinc distribution and accumulation in the topsoil while As and Pb mostly revealed a homogeneous distribution with low metal content.
- In the group of soils derived from soft limestone, As and Pb were mostly characterized by a low level and homogeneous distribution whereas Ni was characterized by a high level and homogeneous distribution. A high level and homogeneous distribution was observed for Cu and a metal increase in the subsoil was observed for Zn.
- In the group of soils derived from volcanic rocks, Ni and Cu were mostly characterized by a high homogeneous distribution and As and Pb were characterized by a low homogeneous distribution. Moreover, Zinc was mostly represented by an accumulation on the soil surface.

In cases where accumulation proved to be concentrated at the surface of the soil, this could be tied to adsorption of metals by clay and O.M or to induced contamination (Duchaufour, 1977). Induced contamination embraces primary sources that include agricultural practices and secondary sources that include smelting activities.

In cases where accumulation proved to be concentrated in the deep layers of the soil profile, this was related to water table contamination, leaching of metals (Anderson, 1877) or soil constituents that adsorb metals (Fenwick and Knapp, 1982) and erosion-deposition processes (Duchaufour, 1977).

CONCLUSION

From the main results obtained throughout this work, additional conclusions can be drawn:

- Basaltic rocks have higher Cu content than calcareous rocks
- Soils derived from volcanic rocks are very abundant in Ni
- Pb content is low in calcareous rocks, and
- As content is low in Volcanic rocks.

It is recommended to:

- Carry future research aiming at studying the bioavailability of heavy metals in different soils.
- Relate the background value with future research on (soil-plant-element) interaction
- Carry research regarding the adaptation of the European criteria for soil pollution to Lebanese soils, and
- Regarding PIXE, further experiments should be carried out in order to improve the detection setup for elements of potential interest, like the use of special X-Rays filters.

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